

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-210319

(43)Date of publication of application : 03.08.2001

(51)Int.Cl. H01M 4/04
C23C 14/14
C23C 16/24
C23C 30/00
H01M 4/02
H01M 4/38

(21)Application number : 2000-018499

(22)Date of filing : 27.01.2000

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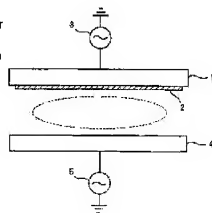
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(54) MANUFACTURING METHOD OF ELECTRODE FOR LITHIUM ION SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To form a silicon thin film on a current collector 2 with a good adhesiveness in a manufacturing method of electrode for lithium secondary battery in which a silicon thin film that forms an active substance on the current collector 2 is formed.

SOLUTION: Ions are made to collide at the current collector 2 when the silicon thin film is formed.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the electrode for lithium secondary batteries which forms the silicon thin film used as an active material on a charge collector.

[0002]

[Description of the Prior Art]In recent years, battery characteristics, such as charge and discharge voltage, charge-and-discharge cycle life property, and a conservation characteristic, are greatly influenced by the electrode for which the lithium secondary battery with which research and development are done briskly is used. From this, improvement in a battery characteristic is achieved by improving an electrode active material.

[0003]When the lithium metal was used as negative electrode active material, per weight and per volume could constitute the cell of the high energy density, but lithium deposited in the shape of a dendrite at the time of charge, and there was a problem of causing an internal short circuit.

[0004]On the other hand, the lithium secondary battery using lithium, aluminum, silicon, tin to alloy, etc. as an electrode is electrochemically reported in the case of charge (SolidState Ionics, 113-115, p57 (1998)). Various rechargeable batteries which especially silicon has large theoretical capacity, are promising as a negative electrode for cells in which high capacity is shown, and make this a negative electrode are proposed among these (JP,10-255768,A). However, sufficient cycle characteristic is not acquired from the alloy itself which is an electrode active material carrying out pulverization of this kind of alloy negative electrode by charge and discharge, and a collecting characteristic getting worse.

[0005]

[Problem(s) to be Solved by the Invention]These people by using the silicon thin film formed on metallic foils, such as copper foil, as a negative electrode for lithium secondary batteries with plasma CVD method etc., Charge-and-discharge capacity found out that it could be considered as the lithium secondary battery which was expensive and was excellent in the charge-discharge cycle characteristic (Japanese Patent Application No. No. 301679 [11 to]).

[0006]In such an electrode for lithium secondary batteries, it is necessary to form the silicon thin film used as an active material with adhesion sufficient on a charge collector. The purpose of this invention is to provide the manufacturing method of the electrode for lithium secondary batteries which can form a silicon thin film with sufficient adhesion on a charge collector.

[0007]

[Means for Solving the Problem]This invention is a manufacturing method of an electrode for lithium secondary batteries which forms a silicon thin film used as an active material on a charge collector, and when it forms a silicon thin film, it is characterized by making ion collide with a charge collector.

[0008]When forming a silicon thin film according to this invention, the adhesion of a silicon thin film to a charge collector can be raised by making ion collide with a charge collector. Ion from plasma is made to collide with a charge collector by impressing negative bias voltage to a charge collector substantially in the 1st aspect of affairs of following this invention. In this case, as a formation method of a silicon thin film, plasma CVD method, sputtering process, etc. are used preferably. As bias voltage impressed to a charge collector, it is more than -100V that it is more than -300V desirable still more preferably.

[0009]As the impression method of voltage, it is impressing direct current voltage, a volts alternating current, or pulse voltage, and negative bias voltage can be impressed substantially and impression of high frequency voltage is used preferably.

[0010]Ion is made to collide with a charge collector by irradiating a charge collector with ion from ion guns in the 2nd aspect of affairs of following this invention. In this case, as a formation method of a silicon thin film, a vacuum deposition method etc. are used preferably. As ion from plasma, and ion from ion guns, at least one sort of ion chosen from argon and hydrogen is mentioned, for example.

[0011]Ion may be made to collide with a charge collector only in an initial stage of thin film forming in the 1st aspect of affairs and 2nd aspect of affairs of following this invention. For example, thickness of a silicon thin film accepts 1 micrometer until it is preferably set to 0.1 micrometer, and it makes ion collide with a charge collector. In the 2nd aspect of affairs of following this invention, ion acceleration voltage and/or ion current density may be decreased with formation of a silicon thin film. Damage which a charge collector receives can be reduced by these.

[0012]As a charge collector in this invention, metallic foils, such as copper foil, are used preferably. Although it can do [using rolled copper foil, electrolytic copper foil, etc. or] as copper foil, from a viewpoint of adhesion, electrolytic copper foil with a

large value of surface roughness Ra is used preferably.

[0013]As a silicon thin film formed in this invention, a microcrystal silicon thin film and an amorphous silicon thin film are preferred. A microcrystal silicon thin film is a silicon thin film in which both a peak near [corresponding to a crystalline region] 520-cm^{-1} and a peak near [corresponding to an amorphous field] 480-cm^{-1} are detected substantially in Raman spectroscopic analysis. An amorphous silicon thin film is a thin film in which a peak near [corresponding to a crystalline region] 520-cm^{-1} is not substantially detected, but a peak near [corresponding to an amorphous field] 480-cm^{-1} is detected substantially in Raman spectroscopic analysis.

[0014]An electrode for lithium secondary batteries manufactured according to this invention can be used as a negative electrode in a lithium secondary battery, and can be used as a lithium secondary battery combining nonaqueous electrolyte and an anode.

[0015]As a solvent of an electrolyte used for a lithium secondary battery, Although not limited in particular, a mixed solvent of cyclic carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate, and chain carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. A mixed solvent of said cyclic carbonate and ether system solvents, such as 1,2-dimethoxyethane and 1,2-dithioxyethane, is also illustrated. As an electrolyte solution, LiPF₆, LiBF₄, LiCF₃SO₃, LiN(CF₃SO₂)₂, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂, LiN(CF₃SO₂)₃ and LiC(C₂F₅SO₂)₃, are illustrated. Furthermore, inorganic solid electrolytes, such as a gel polymer electrolyte with which polymer electrolytes, such as polyethylene oxide and polyacrylonitrile, were impregnated in an electrolysis solution, LiI, Li₂N, Li₃N, are illustrated as an electrolyte.

[0016]As positive active material of a lithium secondary battery, LiCoO₂, LiNiO₂, LiMn₂O₄, LiMnO₂, LiCo_{0.5}Ni_{0.5}O₂, Lithium containing transition metal oxides, such as LiNi_{0.7}Co_{0.2}Mn_{0.1}O₂ and a metallic oxide which does not contain lithium, such as MnO₂, are illustrated. In addition, if it is a substance electrochemically inserted and desorbed from lithium, it can use without restriction.

[0017]

[Embodiment of the Invention]Although this invention is hereafter explained still in detail based on an example, in the range which is not limited to the following examples at all and does not change the gist, it changes suitably and this invention can be carried out.

[0018](Experiment 1) The microcrystal silicon thin film was formed on copper foil with plasma CVD method, using rolled copper foil (18 micrometers in thickness) as a charge collector used as a substrate. Drawing 1 is an outline lineblock diagram showing the plasma CVD device used for formation of this silicon thin film. On the electrode 1 which built in the heater, the copper foil 2 used as a substrate is held. RF generator 3 for impressing negative bias voltage to the copper foil 2 is connected to the electrode 1. The electrode 1 is countered, the counterelectrode 4 is formed and RF generator 5 for generating plasma between the electrode 1 and the counterelectrode 4 is connected to this counterelectrode 4.

[0019]The microcrystal silicon thin film was made to deposit on condition of silane gas flow 10sccm, hydrogen gas flow 200sccm, the substrate temperature of 180 **, the reaction pressure of 40 Pa, and the high-frequency power 555W by RF generator 5 using the device shown in drawing 1 until it became 10 micrometers of thickness on the copper foil 2.

[0020]When making a silicon thin film deposit, as shown in Table 1, bias voltage was impressed to the copper foil 2 which is a substrate from RF generator 3, and the ion from plasma by which it was generated between the electrode 1 and the counterelectrode 4 was made to collide with the copper foil 2. The thin film was made to form about Examples 1 and 2 in the state where impress bias voltage until thickness is set to 0.1 micrometer, and bias voltage is not impressed after that. About Example 3, bias voltage was impressed until it became 10 micrometers to the end of thin film forming (i.e., thickness). About the comparative example 1, the thin film was formed in the state where bias voltage is not impressed.

[0021]Adhesion was evaluated about the copper foil which formed the silicon thin film as mentioned above. The valuation method started 100 samples from copper foil in which the silicon thin film was formed, it is 1 kg of load, and it did the Vickers indenter indentation test, asked for the generated number of the sample which exfoliated, and evaluated it as an exfoliation incidence rate. An evaluation result is shown in Table 1.

[0022][Production of a negative electrode] Copper foil in which the silicon thin film was formed was pierced so that it might be set to 17 mm in diameter, and each negative electrode was produced.

[0023][Production of an anode] Li₂CO₃ and CoCO₃ are used as a starting material, Weighing was carried out and it mixed with the mortar so that the atomic ratio of Li:Co might be set to 1:1, and after pressing and carrying out pressing of this with a metallic mold 17 mm in diameter, in the air, it calcinated at 800 ** for 24 hours, and the baking body of LiCoO₂ was obtained. This was ground until it became the mean particle diameter of 20 micrometers with the mortar.

[0024]Acetylene black as 80 weight sections and a conducting material was mixed so that the polytetrafluoroethylene as ten weight sections and a binder might serve as ten weight sections, and it pressed and carried out pressing with a metallic mold 17 mm in diameter, and the obtained LiCoO₂ powder produced the anode of the pellet type.

[0025][Production of an electrolysis solution] 1 mol/l. of LiPF₆ was dissolved in the constant volume mixed solvent of ethylene carbonate and diethyl carbonate, the electrolysis solution was produced to it, and this was used for it in production of the following cells.

[0026][Production of a cell, and measurement of a charge-discharge cycle characteristic] The flat type lithium secondary battery was produced using the negative electrode, anode, and electrolysis solution which were produced by making it above.

[0027]it charged until negative-electrode capacity became 2000 mAh/g with the current value A of 100micro in 25 ** about the produced lithium secondary battery -- the afterdischarge was carried out, this was made into the charge and discharge of one cycle, and the capacity maintenance rate of 50 cycle eye was measured about each cell. A measurement result is shown in Table 1.

[0028]

Table 1]

	実施例 1	実施例 2	実施例 3	比較例 1
印加電圧	-100V	-800V	-100V	0V (未印加)
電圧印加時間 (膜厚)	0.1 μ m	0.1 μ m	10 μ m	-
集電体の状態	変化なし	変化なし	腐性が低下	変化なし
密着性 (剝離発生率)	6%	5%	-	24%
50サイクル目の 容量維持率	99%	91%	-	85%

[0029]As shown in Table 1, in the case of silicon thin film formation, negative bias voltage is impressed to copper foil which is a charge collector, and Example 1 and Example 2 which made the ion from plasma collide with a charge collector show good adhesion compared with the comparative example 1. The good capacity maintenance rate is shown also in the charge-discharge cycle characteristic. In Example 3, since the toughness of the charge collector was falling, evaluation of the charge-discharge cycle characteristic which produces an adhesion test and a cell was not performed.

[0030](Experiment 2) The amorphous silicon thin film was formed on copper foil by sputtering process using the same copper foil as the experiment 1. Drawing 2 is an outline lineblock diagram of the sputter device used for formation of this silicon thin film. As shown in drawing 2, the composition of a sputter device is the same as that of the plasma CVD device used in the experiment 1, and it differs in that the silicon target 10 is installed on the counterelectrode 9.

[0031]The amorphous silicon thin film was made to deposit using the device shown in drawing 2 until it became 10 micrometers of thickness on the copper foil 7 on condition of argon gas flow 100sccm, a substrate temperature:room temperature (with un-heating and no temperature control), the reaction pressure of 0.1 Pa, and the high-frequency power 200W by RF generator 11.

[0032]The ion from plasma by which it was generated between the electrode 6 and the counterelectrode 9 was made to collide with the copper foil 7 by impressing bias voltage to the copper foil 7 which is a substrate from RF generator 8 like the experiment 1. The thin film was made to form in Example 4 in the state where impress bias voltage until thickness is set to 0.1 micrometer, and bias voltage is not impressed after that. About the comparative example 2, the thin film was formed in the state where bias voltage is not impressed.

[0033]About the copper foil which formed the silicon thin film as mentioned above, the adhesion test and the charge-discharge cycle characteristic by cell production were evaluated like the experiment 1. A result is shown in Table 2.

[0034]

Table 2]

	実施例 4	比較例 2
印加電圧	-100V	0V (未印加)
電圧印加時間 (膜厚)	0.1 μ m	-
集電体の状態	変化なし	変化なし
密着性 (剝離発生率)	4%	10%
50サイクル目の 容量維持率	98%	95%

[0035]Example 4 according to this invention shows good adhesion compared with the comparative example 2 so that clearly from the result shown in Table 2. The good capacity maintenance rate is shown also in the charge-discharge cycle characteristic.

[0036](Experiment 3) The amorphous silicon thin film was made to deposit on copper foil with a vacuum deposition method, making the ion from ion guns collide with copper foil using the same copper foil as the experiment 1. Drawing 3 is an outline lineblock diagram showing the vacuum evaporator used for this silicon thin film formation. The copper foil 22 which is a substrate is held on the substrate holder 21. The deposition source 23 which equipped the substrate holder 21 and the position which counters with electron beam (EB) cancer is established. The ion guns 24 are formed in the position which can irradiate with ion to the copper foil 22.

[0037]Ar gas is introduced in a chamber by the flow of 5sccm from the ion guns 24, and the amorphous silicon thin film was made to deposit until thickness was set to 10 micrometers on the copper foil 22 on having no substrate temperature:heating

(about 40^{**}) and conditions with an evaporation rate of 10A/second. The ion acceleration voltage of the ion guns 24 is set up, it irradiated with Ar^{+} ion on the copper foil 22, and it was made to collide in the case of silicon thin film deposition, as shown in Table 3. Ion current density was set up within the limits of $0.4\text{--}5\text{mA}/\text{cm}^2$ according to accelerating voltage. [0038]About Examples 5, 7, 8, and 9, it irradiated with ion until the thickness of the silicon thin film was set to 0.1 micrometer, as shown in Table 3, and it did not irradiate with ion after that. About Example 6, it irradiated with ion until it became 10 micrometers to the end of thin film forming (i.e., thickness).

[0039]About the copper foil which formed the silicon thin film as mentioned above, the adhesion test and the charge-discharge cycle characteristic by cell production were evaluated like the experiment 1. A result is shown in Table 3.

[0040]

[Table 3]

	実施例 5	実施例 6	実施例 7	実施例 8	実施例 9
イオン種と加速電圧	Ar^{+} 0 0 0 V	Ar^{+} 0 0 0 V	Ar^{+} 5 k V	Ar^{+} 1 0 k V	Ar^{+} 1 2 k V
電圧印加時間 (標準)	0. 1 μm	1 0 μm	0. 1 μm	0. 1 μm	0. 1 μm
集電体の状態	変化なし	変化なし	変化なし	変化なし	劣化が低下
密着性 (剥離発生率)	2 %	2 %	0 %	0 %	—
50サイクル目の容量維持率	0 0 %	6 0 %	8 2 %	6 2 %	—

[0041]While good adhesion is acquired in Examples 5-8 in which the silicon thin film was formed, making ion collide according to this invention so that clearly from the result shown in Table 3, the good charge-discharge cycle characteristic is obtained. In Example 9, since the toughness of the charge collector was falling, evaluation of the adhesion test and the charge-discharge cycle characteristic was not performed.

[0042](Experiment 4) The amorphous silicon thin film was made to deposit on a charge collector, making the ion from ion guns collide with a charge collector using the same vacuum evaporator as the experiment 3, using the same copper foil as the experiment 1 as a charge collector until it became 10 micrometers of thickness.

[0043]As shown in Table 4, about Example 10, Ar gas 5scm, H_2 gas was introduced in the chamber from ion guns by the flow of 5scm, accelerating voltage was set to 900V, ion current density was made into $0.4\text{ mA}/\text{cm}^2$, and the thin film was formed, irradiating with the ion from ion guns until it was set to 10 micrometers to the end of thin film forming (i.e., thickness).

[0044]The silicon thin film was made to deposit about Example 11, until the thickness of a silicon thin film is set to 1 micrometer, as shown in Table 4, decreasing accelerating voltage linearly from 5kv to 0V. Ion current density was linearly decreased from $3\text{ mA}/\text{cm}^2$ to $0\text{ mA}/\text{cm}^2$ with reduction in accelerating voltage.

[0045]About the copper foil which formed the silicon thin film as mentioned above, the adhesion test and the charge-discharge cycle characteristic by cell production were evaluated like the experiment 1. A result is shown in Table 4.

[0046]

[Table 4]

	実施例 1 0	実施例 1 1
イオン種と加速電圧	Ar^{+} H^{+} 0 0 0 V	Ar^{+} 5 k V ~ 0 V
電圧印加時間 (標準)	1 0 μm	1 μm
集電体の状態	変化なし	変化なし
密着性 (剥離発生率)	1 %	0 %
50サイクル目の容量維持率	6 1 %	6 2 %

[0047]As shown in Table 4, while good adhesion is acquired in Examples 10 and 11 according to this invention, the good charge-discharge cycle characteristic is obtained.

[0048]

[Effect of the Invention]According to this invention, a silicon thin film can be formed with sufficient adhesion on a charge collector, and the electrode for lithium secondary batteries excellent in the charge-discharge cycle characteristic can be manufactured.

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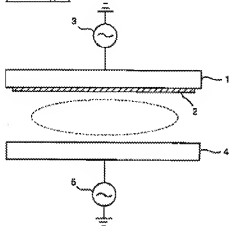
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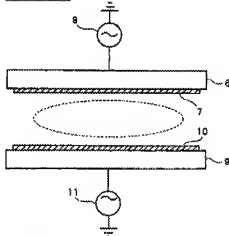
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DRAWINGS

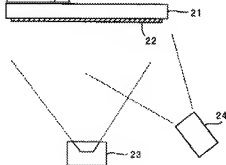
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]